



# Crystal structure of *trans*-bis(diethanolamine- $\kappa^3O,N,O'$ )manganese(II) bis(3-aminobenzoate)

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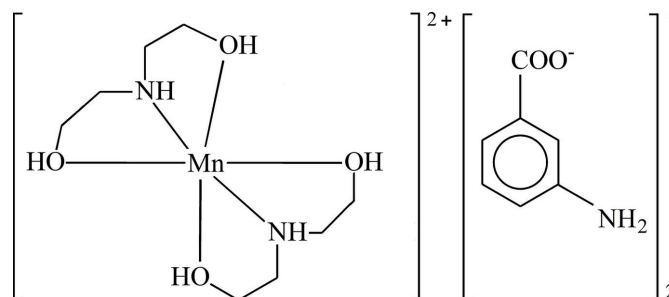
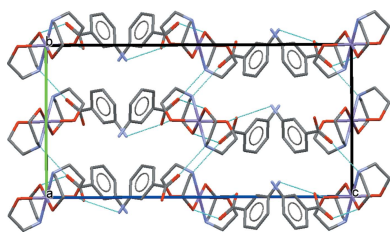
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Reaction of *m*-aminobenzoic acid (MABA), diethanolamine (DEA) and  $MnCl_2 \cdot 4H_2O$  led to the formation of the title salt,  $[Mn(C_4H_{11}NO_2)_2]-(C_7H_6NO_2)_2$ . In the complex cation, the  $Mn^{2+}$  ion is located on an inversion centre and is coordinated by two symmetry-related tridentate DEA molecules, leading to the formation of a slightly distorted  $MnN_2O_4$  octahedron. The  $MABA^-$  counter-anions are connected to the complex ion by a pair of rather strong  $O-H \cdots O$  hydrogen bonds, yielding a 1:2 supramolecular aggregate. Much weaker  $N-H \cdots O$  hydrogen bonds connect neighbouring aggregates into a three-dimensional network structure.

## 1. Chemical context

In contrast to the two other isomers of aminobenzoic acid, *viz.* *p*-aminobenzoic acid (or vitamin B<sub>10</sub>) and *o*-aminobenzoic acid (or antranilic acid), *m*-aminobenzoic acid (3-aminobenzoic acid or MABA) is not biologically active. Nevertheless, we are studying this substance within the context of mixed-ligand coordination complex formation including benzoic acid isomers and ethanolamines (Ashurov *et al.*, 2015). As a result of the presence of two spatially separated electron-donor functional groups in the MABA molecule, the reported metal complexes of this ligand are mostly coordination polymers. Polymerization may take place involving both COOH and NH<sub>2</sub> functional groups (Wang *et al.*, 2004; Flemig *et al.*, 2008; Tan *et al.*, 2006; Wei *et al.*, 2006; Shen & Lush, 2010; Wang *et al.*, 2006;), or only one of them: COOH (Kozioł *et al.*, 1992; Murugavel & Banerjee, 2003; Flemig *et al.*, 2008; Tsaryuk *et al.*, 2014) or, more infrequently, NH<sub>2</sub> (Wang *et al.*, 2004).



In discrete monoligand complexes, the MABA molecules coordinate to metal ions only bidentately through the oxygen atoms of the carboxylic group (Ozhafarov *et al.*, 1981) while in mixed-ligand complexes, the carboxylic group can feature mono- (Sundberg *et al.*, 1998;) or bidentate (Palanisami *et al.*,

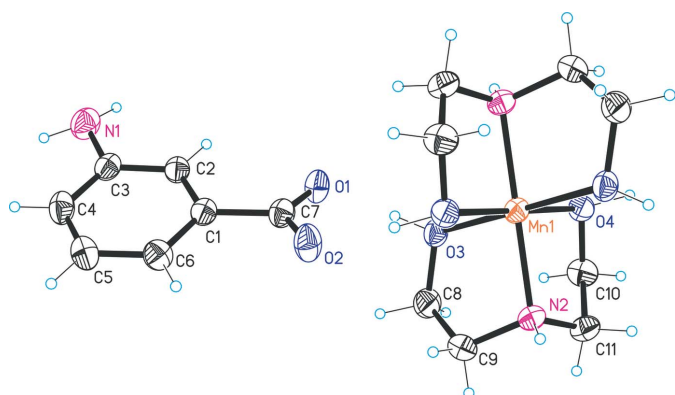


Figure 1

The structures of the molecular moieties in the title salt. Displacement ellipsoids are drawn at the 50% probability level and the asymmetric unit is identified by the numbering of its atoms.

2013) coordination modes. Coordination through the nitrogen atom is observed only in an Ag complex with participation of the co-ligand *p*-toluenesulfonate (Smith *et al.*, 1998).

The disposition of MABA molecules as non-coordinating counter-ions (in their benzoate form) is characteristic for mixed-ligand Mn (Fang & Nie, 2011) or Cd complexes (Gao *et al.*, 2011) with 4,4-bipyridine as co-ligand whereas the simultaneous presence of coordinating and non-coordinating MABA species was reported for an Mn complex with 1,10-phenanthroline as an additional ligand (Zhang, 2006).

Diethanolamine (DEA) ligands can coordinate to metal ions in a mono- (Petrović *et al.*, 2006), bi- (Yilmaz *et al.*, 2000) or tridentate (Buvaylo *et al.*, 2009) mode if two ligand molecules are situated around the central atom. However, a combination of these modes, for example, in a bi- and tridentate fashion, is also possible (Bertrand *et al.*, 1979).

A search in the Cambridge Structural Database (CSD; Groom & Allen, 2014) revealed that crystal structures have been reported for complexes of MABA and DEA with many metal ions, including zinc, copper, nickel, manganese, cadmium, cobalt, *etc.* However, no mixed-ligand metal complex including MABA and DEA is documented in the CSD. In order to prepare such compounds, we carried out a synthesis in a solution containing an Mn salt, MABA and DEA. Instead of the desired complex, the title salt,  $[\text{Mn}(\text{C}_4\text{H}_{11}\text{NO}_2)_2](\text{C}_7\text{H}_6\text{NO}_2)_2$ , consisting of discrete  $[\text{Mn}(\text{DEA})_2]^{2+}$  cations and  $\text{MABA}^-$  anions was obtained.

## 2. Structural commentary

The asymmetric unit consists of one DEA ligand, one  $\text{MABA}^-$  anion and one  $\text{Mn}^{2+}$ -ion, the latter being located on an inversion centre (Fig. 1). Coordination of the DEA ligand to the metal ion takes place in a tridentate *O,N,O'* mode. The Mn–ligand bond lengths cover a range from 2.065 (2) to 2.096 (2) Å with an angular range of 81.79 (10) to 98.21 (10)°, leading to a slightly distorted  $\text{MnN}_2\text{O}_4$  octahedron. Since the DEA ligands are in their neutral form, a charged component in the outer sphere is required for charge compensation.

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N2–H2···O2 <sup>i</sup>	0.96 (3)	2.19 (3)	2.965 (4)	137 (3)
N1–H1A···O1 <sup>ii</sup>	0.97 (2)	2.05 (2)	3.008 (4)	170 (5)
O4–H4···O2 <sup>iii</sup>	0.99 (5)	1.63 (5)	2.611 (3)	169 (4)
O3–H3···O1	0.92 (6)	1.65 (6)	2.562 (3)	173 (5)

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (ii)  $x + \frac{1}{2}, y, -z + \frac{3}{2}$ ; (iii)  $-x + 1, -y + 1, -z + 1$ .

Hence, two  $\text{MABA}^-$  anions in the benzoate form are present per complex ion. The carboxylate group of the anionic molecule is tilted by 14.4 (4)° relative to the aromatic ring.

## 3. Supramolecular features

The  $\text{MABA}^-$  anion is connected to the complex ion by a pair of rather strong  $\text{O–H} \cdots \text{O}$  hydrogen bonds involving the DEA hydroxy groups [2.562 (3) and 2.611 (3) Å; Table 1], which give rise to the formation of a supramolecular motif with graph-set notation  $R_2^2(8)$ . The resulting supramolecular cationic:anionic 1:2 units are associated to other such units by relatively weak  $\text{N–H} \cdots \text{O}$  hydrogen bonds [2.965 (4) and 3.008 (4) Å; Table 1] involving the secondary amine function of the DEA ligand and one of the H atoms of the  $\text{MABA}^-$  amino group; notably, the second H atom (H1B) of the amino group remains without an acceptor. These four hydrogen bonds associate the different moieties into a three-dimensional network (Fig. 2).

## 4. Synthesis and crystallization

To an aqueous solution (5 ml) of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.098 g, 0.5 mmol) was slowly added an ethanolic solution (5 ml) containing DEA (96 µl) and MABA (0.137 g, 1 mmol) under constant stirring. A light-pink crystalline product was obtained at room temperature by solvent evaporation after 20 days.

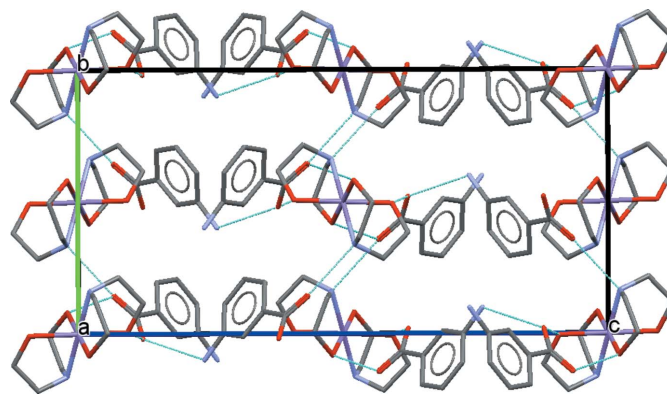


Figure 2

The crystal packing in the title structure. Hydrogen bonds are shown as dashed lines.

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The positions of the O- and N-bound hydrogen atoms were located from difference Fourier maps. Whereas O-bound hydrogen atoms were refined freely, N-bound H atoms were refined with soft distance restraints of 0.98 Å for the secondary amine function and of 0.95 Å for the primary amine function. The C-bound hydrogen atoms were placed in calculated positions and refined as riding atoms with C–H = 0.93 and 0.97 Å for aromatic and methylene hydrogen atoms, respectively, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

## Acknowledgements

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Table 2

Experimental details.

Crystal data	
Chemical formula	[Mn(C <sub>4</sub> H <sub>11</sub> NO <sub>2</sub> ) <sub>2</sub> ](C <sub>7</sub> H <sub>6</sub> NO <sub>2</sub> ) <sub>2</sub>
<i>M<sub>r</sub></i>	537.47
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.6120 (4), 10.8219 (4), 21.7591 (8)
<i>V</i> (Å <sup>3</sup> )	2498.86 (15)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
<i>μ</i> (mm <sup>-1</sup> )	4.76
Crystal size (mm)	0.32 × 0.20 × 0.18
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Ruby
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.932, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	10631, 2589, 1740
<i>R<sub>int</sub></i>	0.056
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.630
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.045, 0.136, 1.06
No. of reflections	2589
No. of parameters	180
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.37, −0.22

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97*, *XP* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *Mercury* (Macrae *et al.*, 2006).

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## supporting information

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## Crystal structure of *trans*-bis(diethanolamine- $\kappa^3O,N,O'$ )manganese(II) bis(3-aminobenzoate)

**Aziz B. Ibragimov, Bakhtiyar S. Zakirov and Jamshid M. Ashurov**

### Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

### *trans*-Bis(diethanolamine- $\kappa^3O,N,O'$ )manganese(II) bis(3-aminobenzoate)

#### Crystal data

$[\text{Mn}(\text{C}_4\text{H}_{11}\text{NO}_2)_2](\text{C}_7\text{H}_6\text{NO}_2)_2$

$M_r = 537.47$

Orthorhombic, *Pbca*

$a = 10.6120$  (4) Å

$b = 10.8219$  (4) Å

$c = 21.7591$  (8) Å

$V = 2498.86$  (15) Å<sup>3</sup>

$Z = 4$

$F(000) = 1132$

$D_x = 1.429$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å

Cell parameters from 1995 reflections

$\theta = 4.1\text{--}75.0^\circ$

$\mu = 4.76$  mm<sup>-1</sup>

$T = 293$  K

Block, pink

$0.32 \times 0.20 \times 0.18$  mm

#### Data collection

Oxford Diffraction Xcalibur Ruby diffractometer

Radiation source: fine-focus sealed X-ray tube

Detector resolution: 10.2576 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.932$ ,  $T_{\max} = 1.000$

10631 measured reflections

2589 independent reflections

1740 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.056$

$\theta_{\max} = 76.3^\circ$ ,  $\theta_{\min} = 4.1^\circ$

$h = -13 \rightarrow 11$

$k = -10 \rightarrow 13$

$l = -23 \rightarrow 27$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.136$

$S = 1.06$

2589 reflections

180 parameters

3 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.8708P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$$

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.5000	0.5000	0.5000	0.04895 (19)
O4	0.3260 (2)	0.5819 (2)	0.52055 (10)	0.0539 (5)
O3	0.5434 (2)	0.4939 (2)	0.59247 (10)	0.0565 (5)
O1	0.7755 (2)	0.5192 (2)	0.62224 (11)	0.0632 (6)
O2	0.8300 (3)	0.3560 (3)	0.56693 (12)	0.0734 (7)
N2	0.4066 (3)	0.3381 (2)	0.52171 (12)	0.0512 (6)
C1	0.9619 (3)	0.4152 (3)	0.64986 (13)	0.0518 (7)
C2	0.9990 (3)	0.5096 (3)	0.68864 (13)	0.0516 (6)
H2A	0.9520	0.5821	0.6899	0.062*
N1	1.1449 (4)	0.5979 (4)	0.76146 (16)	0.0793 (10)
C7	0.8479 (3)	0.4310 (3)	0.60979 (14)	0.0547 (7)
C3	1.1051 (3)	0.4986 (4)	0.72582 (13)	0.0566 (7)
C6	1.0307 (3)	0.3059 (4)	0.64803 (16)	0.0617 (8)
H6	1.0069	0.2422	0.6218	0.074*
C4	1.1723 (3)	0.3888 (4)	0.72398 (15)	0.0659 (9)
H4A	1.2432	0.3795	0.7487	0.079*
C11	0.2710 (3)	0.3669 (3)	0.53064 (17)	0.0618 (8)
H11A	0.2348	0.3081	0.5592	0.074*
H11B	0.2272	0.3586	0.4917	0.074*
C5	1.1356 (3)	0.2928 (4)	0.68595 (16)	0.0682 (9)
H5	1.1811	0.2193	0.6857	0.082*
C10	0.2524 (4)	0.4967 (3)	0.55517 (17)	0.0657 (9)
H10A	0.1640	0.5191	0.5525	0.079*
H10B	0.2772	0.4999	0.5980	0.079*
C9	0.4717 (4)	0.2849 (3)	0.57585 (18)	0.0690 (10)
H9A	0.5494	0.2457	0.5628	0.083*
H9B	0.4187	0.2222	0.5944	0.083*
C8	0.5008 (4)	0.3832 (4)	0.62248 (16)	0.0724 (10)
H8A	0.4259	0.4010	0.6464	0.087*
H8B	0.5656	0.3537	0.6503	0.087*
H4	0.276 (5)	0.606 (5)	0.484 (2)	0.099 (15)*
H2	0.429 (4)	0.278 (3)	0.4912 (14)	0.071 (11)*
H3	0.628 (6)	0.501 (5)	0.600 (3)	0.109 (18)*
H1A	1.196 (5)	0.571 (6)	0.7962 (18)	0.13 (2)*
H1B	1.087 (6)	0.664 (5)	0.771 (3)	0.18 (3)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mn1	0.0487 (3)	0.0479 (3)	0.0503 (3)	-0.0033 (3)	-0.0032 (3)	-0.0027 (3)
O4	0.0536 (11)	0.0496 (11)	0.0586 (12)	0.0035 (10)	-0.0011 (10)	-0.0037 (10)
O3	0.0553 (12)	0.0658 (14)	0.0485 (10)	-0.0038 (11)	-0.0093 (9)	-0.0029 (11)
O1	0.0529 (12)	0.0758 (16)	0.0608 (12)	0.0082 (11)	-0.0109 (10)	-0.0144 (12)
O2	0.0762 (16)	0.0790 (17)	0.0650 (14)	0.0167 (14)	-0.0226 (12)	-0.0215 (13)
N2	0.0540 (14)	0.0457 (13)	0.0539 (13)	-0.0065 (11)	0.0018 (11)	-0.0061 (11)
C1	0.0494 (15)	0.0631 (18)	0.0429 (13)	-0.0042 (14)	0.0023 (12)	0.0026 (14)
C2	0.0465 (14)	0.0632 (17)	0.0452 (13)	-0.0017 (14)	0.0025 (11)	0.0061 (14)
N1	0.077 (2)	0.094 (3)	0.0674 (19)	-0.014 (2)	-0.0126 (16)	-0.0015 (19)
C7	0.0504 (16)	0.064 (2)	0.0496 (16)	-0.0016 (15)	-0.0012 (12)	-0.0024 (14)
C3	0.0520 (16)	0.073 (2)	0.0448 (13)	-0.0117 (16)	0.0003 (12)	0.0032 (16)
C6	0.067 (2)	0.065 (2)	0.0535 (16)	0.0017 (17)	-0.0015 (14)	-0.0011 (16)
C4	0.0520 (17)	0.094 (3)	0.0522 (17)	0.0043 (19)	-0.0040 (14)	0.0079 (18)
C11	0.0559 (19)	0.0569 (18)	0.073 (2)	-0.0107 (15)	0.0060 (15)	-0.0005 (16)
C5	0.063 (2)	0.079 (2)	0.0622 (19)	0.0150 (18)	-0.0014 (15)	0.0056 (18)
C10	0.0606 (19)	0.066 (2)	0.071 (2)	0.0055 (18)	0.0172 (16)	0.0018 (19)
C9	0.077 (2)	0.0563 (19)	0.074 (2)	-0.0046 (17)	-0.0092 (18)	0.0154 (17)
C8	0.076 (2)	0.088 (3)	0.0533 (18)	-0.014 (2)	-0.0086 (17)	0.0136 (19)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Mn1—O3 <sup>i</sup>	2.065 (2)	N1—C3	1.391 (5)
Mn1—O3	2.065 (2)	N1—H1A	0.97 (2)
Mn1—N2	2.067 (3)	N1—H1B	0.97 (2)
Mn1—N2 <sup>i</sup>	2.068 (3)	C3—C4	1.387 (5)
Mn1—O4	2.096 (2)	C6—C5	1.393 (5)
Mn1—O4 <sup>i</sup>	2.096 (2)	C6—H6	0.9300
O4—C10	1.424 (4)	C4—C5	1.384 (6)
O4—H4	0.99 (5)	C4—H4A	0.9300
O3—C8	1.438 (4)	C11—C10	1.515 (5)
O3—H3	0.92 (6)	C11—H11A	0.9700
O1—C7	1.255 (4)	C11—H11B	0.9700
O2—C7	1.251 (4)	C5—H5	0.9300
N2—C9	1.482 (4)	C10—H10A	0.9700
N2—C11	1.485 (4)	C10—H10B	0.9700
N2—H2	0.959 (19)	C9—C8	1.502 (5)
C1—C2	1.383 (5)	C9—H9A	0.9700
C1—C6	1.390 (5)	C9—H9B	0.9700
C1—C7	1.501 (4)	C8—H8A	0.9700
C2—C3	1.391 (4)	C8—H8B	0.9700
C2—H2A	0.9300		
O3 <sup>i</sup> —Mn1—O3	180.00 (14)	O1—C7—C1	117.0 (3)
O3 <sup>i</sup> —Mn1—N2	98.21 (10)	C4—C3—N1	121.5 (3)
O3—Mn1—N2	81.79 (10)	C4—C3—C2	118.2 (3)

O3 <sup>i</sup> —Mn1—N2 <sup>i</sup>	81.79 (10)	N1—C3—C2	120.3 (4)
O3—Mn1—N2 <sup>i</sup>	98.21 (10)	C1—C6—C5	119.3 (4)
N2—Mn1—N2 <sup>i</sup>	180.0	C1—C6—H6	120.4
O3 <sup>i</sup> —Mn1—O4	89.88 (9)	C5—C6—H6	120.4
O3—Mn1—O4	90.12 (9)	C5—C4—C3	121.1 (3)
N2—Mn1—O4	83.54 (10)	C5—C4—H4A	119.5
N2 <sup>i</sup> —Mn1—O4	96.46 (10)	C3—C4—H4A	119.5
O3 <sup>i</sup> —Mn1—O4 <sup>i</sup>	90.11 (9)	N2—C11—C10	111.6 (3)
O3—Mn1—O4 <sup>i</sup>	89.89 (9)	N2—C11—H11A	109.3
N2—Mn1—O4 <sup>i</sup>	96.47 (10)	C10—C11—H11A	109.3
N2 <sup>i</sup> —Mn1—O4 <sup>i</sup>	83.53 (10)	N2—C11—H11B	109.3
O4—Mn1—O4 <sup>i</sup>	180.0	C10—C11—H11B	109.3
C10—O4—Mn1	108.80 (19)	H11A—C11—H11B	108.0
C10—O4—H4	107 (3)	C4—C5—C6	120.2 (4)
Mn1—O4—H4	115 (3)	C4—C5—H5	119.9
C8—O3—Mn1	113.5 (2)	C6—C5—H5	119.9
C8—O3—H3	108 (3)	O4—C10—C11	110.0 (3)
Mn1—O3—H3	113 (4)	O4—C10—H10A	109.7
C9—N2—C11	115.4 (3)	C11—C10—H10A	109.7
C9—N2—Mn1	106.7 (2)	O4—C10—H10B	109.7
C11—N2—Mn1	108.5 (2)	C11—C10—H10B	109.7
C9—N2—H2	100 (2)	H10A—C10—H10B	108.2
C11—N2—H2	118 (3)	N2—C9—C8	110.9 (3)
Mn1—N2—H2	108 (2)	N2—C9—H9A	109.4
C2—C1—C6	119.8 (3)	C8—C9—H9A	109.4
C2—C1—C7	120.0 (3)	N2—C9—H9B	109.4
C6—C1—C7	120.2 (3)	C8—C9—H9B	109.4
C1—C2—C3	121.5 (3)	H9A—C9—H9B	108.0
C1—C2—H2A	119.3	O3—C8—C9	110.4 (3)
C3—C2—H2A	119.3	O3—C8—H8A	109.6
C3—N1—H1A	112 (4)	C9—C8—H8A	109.6
C3—N1—H1B	119 (5)	O3—C8—H8B	109.6
H1A—N1—H1B	114 (5)	C9—C8—H8B	109.6
O2—C7—O1	124.2 (3)	H8A—C8—H8B	108.1
O2—C7—C1	118.8 (3)		
C6—C1—C2—C3	0.7 (5)	C2—C3—C4—C5	0.4 (5)
C7—C1—C2—C3	-179.2 (3)	C9—N2—C11—C10	88.9 (4)
C2—C1—C7—O2	166.2 (3)	Mn1—N2—C11—C10	-30.7 (3)
C6—C1—C7—O2	-13.6 (5)	C3—C4—C5—C6	0.9 (6)
C2—C1—C7—O1	-14.4 (5)	C1—C6—C5—C4	-1.4 (5)
C6—C1—C7—O1	165.7 (3)	Mn1—O4—C10—C11	-38.9 (3)
C1—C2—C3—C4	-1.2 (5)	N2—C11—C10—O4	47.5 (4)
C1—C2—C3—N1	175.9 (3)	C11—N2—C9—C8	-76.9 (4)
C2—C1—C6—C5	0.7 (5)	Mn1—N2—C9—C8	43.7 (4)

C7—C1—C6—C5	-179.5 (3)	Mn1—O3—C8—C9	17.4 (4)
N1—C3—C4—C5	-176.6 (3)	N2—C9—C8—O3	-40.8 (4)

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N2—H2...O2 <sup>ii</sup>	0.96 (3)	2.19 (3)	2.965 (4)	137 (3)
N1—H1A...O1 <sup>iii</sup>	0.97 (2)	2.05 (2)	3.008 (4)	170 (5)
O4—H4...O2 <sup>i</sup>	0.99 (5)	1.63 (5)	2.611 (3)	169 (4)
O3—H3...O1	0.92 (6)	1.65 (6)	2.562 (3)	173 (5)

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x-1/2, -y+1/2, -z+1$ ; (iii)  $x+1/2, y, -z+3/2$ .